MEMBRANE SEPARATIONS

Bipolar Membranes and Membrane Processes

H. Strathmann, University of Twente, The Netherlands

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Bipolar membranes are gaining increasing attention as an efficient tool for the production of acids and bases from the corresponding salts by electrodialytic water dissociation. The process is economically very attractive and has a multitude of interesting potential applications. The large scale utilization of bipolar membranes, however, is still limited today by unsatisfactory membrane properties and by a lack of application know-how. A bipolar membrane should have adequate water dissociation capability, low electrical resistance, high permselectivity and a long useful life under operating conditions, which means that it must be stable in highly concentrated acid or alkaline solutions. The monopolar anion and cation exchange membranes which are also needed in the process should have good proton and hydroxide ion-blocking capability in addition to stability in strong bases and acids.

Although today's membranes do not meet all of these required properties, they are used successfully in a number of relevant applications.

The Principle of Electrodialytic Water Dissociation

The process of electrodialytic water dissociation using a bipolar membrane is illustrated in **Figure 1**, which shows a bipolar membrane consisting of cation and anion exchange layers arranged in parallel between two electrodes. If an electrical potential difference is established between the electrodes, charged species are removed from the interphase between the

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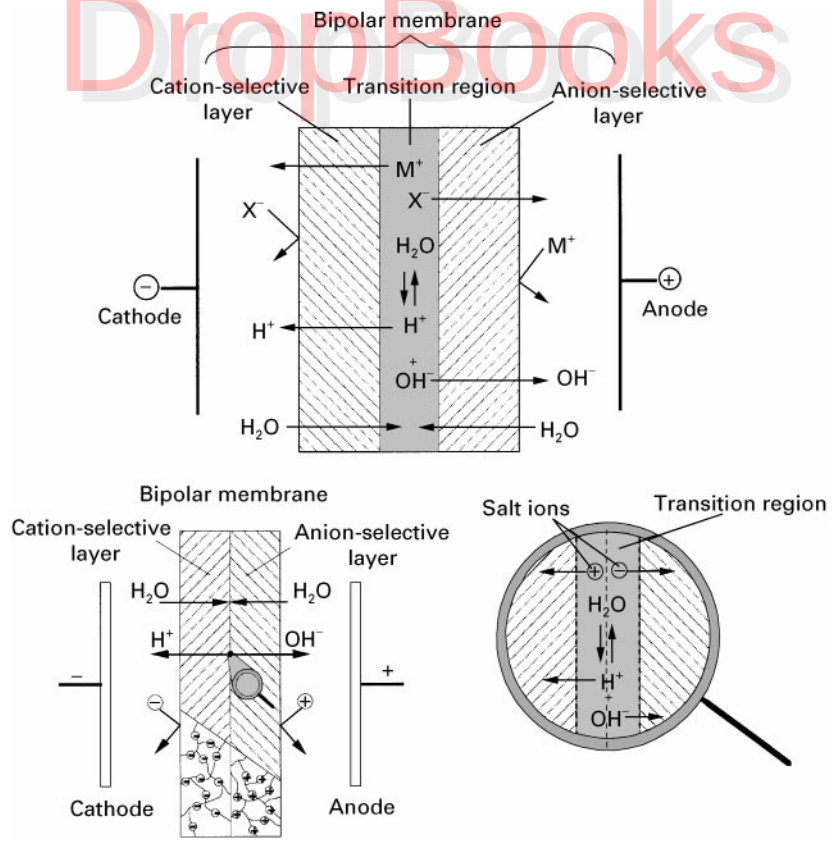

Figure 1 Schematic diagram illustrating the principle of electrodialytic water dissociation in bipolar membranes.

two ion exchange layers. When all salt ions are removed from the interphase region, further transport of electrical charges can only be accomplished by protons and hydroxide ions, which are available in a concentration of *ca.* 1×10^{-7} mol L^{-1}. Bipolar membranes resemble a laminate of a cation and an anion exchange layer with a very thin (4–5 nm) transition region in which the water dissociation occurs according to the water dissociation equilibrium given by:

$$2H_2O \rightleftarrows H_3O^+ + OH^- \qquad [1]$$

The reversible energy required for the production of acids and bases in a bipolar membrane at constant temperature and pressure can be calculated by the Nernst equation for a concentration chain of solutions with different H^+ ion activities, i.e. pH values:

$$\Delta G = F \cdot \Delta U = 2.3\, RT\, \Delta pH \qquad [2]$$

Here ΔG is the reversible Gibb's free energy, ΔU the electrical potential difference between the two solutions, R is the gas constant, T is the absolute temperature, F is the Faraday constant, and ΔpH is the difference between the pH values of the two solutions separated by the bipolar membrane. For 1 mol L^{-1} acid and base solutions in the two phases separated by the membrane, ΔU is 0.8 V and ΔG is 0.02 kWh mol^{-1} at 25°C.

The potential drop across the bipolar membrane measured in a water dissociation experiment is always higher than the calculated theoretical value because of irreversible effects due to the electrical resistance of the membrane and the solutions.

To utilize bipolar membranes for the production of acids and bases from the corresponding salt solution they must be combined with monopolar ion exchange membranes, as illustrated in **Figure 2**. This schematic drawing shows bipolar and cation and anion

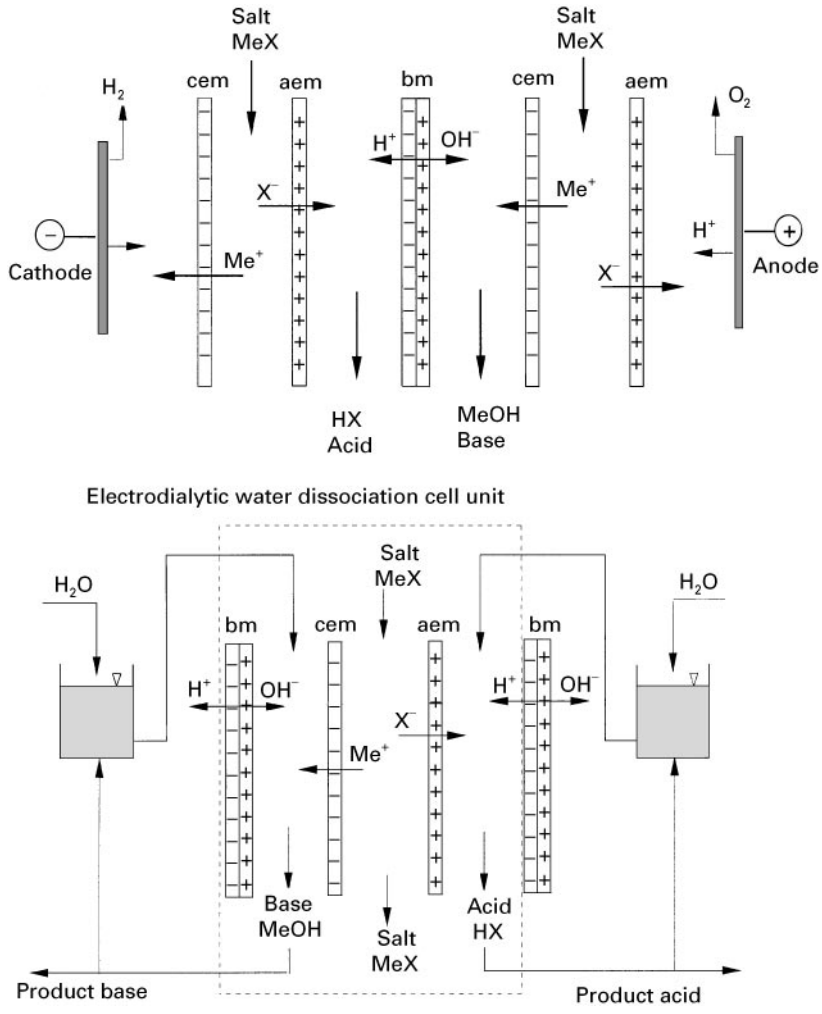

Figure 2 Schematic drawing illustrating the principle of electrodialytic production of acids and bases from the corresponding salts with bipolar membranes.

exchange membranes arranged in parallel between two electrodes to form individual compartments. The electrodialysis cell arrangement consists of three individual compartments and three membranes, i.e. the bipolar and the cation and anion exchange membrane. As in conventional electrodialysis, a large number of the three-compartment units can be stacked between electrodes. When a salt solution is introduced in the middle compartment and an electrical potential difference between the electrodes is established, the cations in the salt solution migrate towards the cathode. They permeate the cation exchange membrane and form a base with the hydroxide ions generated in the bipolar membrane. On the other side of the bipolar membrane protons, which are generated simultaneously with the hydroxide ions, form an acid with anions migrating from the salt solution through the anion exchange membrane towards the anode. The net result of the process is the production of an acid and a base from the corresponding salt solution.

The Mechanism of Water Dissociation in Bipolar Membranes

The water dissociation rate in the bipolar membrane determines the overall efficiency of the process. It can easily be shown, however, that the dissociation rate constant of pure water is much too low to explain the experimentally determined high acid and base generation rate in bipolar membranes.

As indicated earlier, a bipolar membrane consists of a laminate of cation and anion exchange layers. The specific resistance σ of a strong acid or base ion exchange layer is in the order of 50–100 Ω cm. Assuming a thickness of 100 μm each for the cation and anion exchange layers, the total area resistance r of the ion exchange layers of the bipolar membrane is in the order of 1–2 $\Omega\,cm^2$.

The electrical resistance of the interphase layer of a bipolar membrane which is assumed to consist of deionized water can be calculated by:

$$r_{in} = \frac{\lambda}{\kappa} \qquad [3]$$

where r_{in} is the area resistance, λ the thickness, and κ is the specific conductivity of the interphase layer. If the interphase layer contains only pure water, its specific resistance is approximately $18 \times 10^6\ \Omega$ cm. Thus, the area resistance of a 1 nm thick interphase is approximately 1.8 $\Omega\,cm^2$. The above argument however is only correct if the ion concentration in the interphase is constant and all ions which are removed by the electric current across the bipolar membrane are replenished by the water dissociation. This means that the ion fluxes from the bipolar membrane into the outer phases cannot exceed the rate of their generation in the interphase. Thus, the maximum flux of H^+ and OH^- ions of the bipolar membrane is given by:

$$J_{H^+} = J_{OH^-} = k_d C_{H_2O}\,\lambda \qquad [4]$$

where J is the maximum ion flux from the bipolar membrane into the outer phases, k_d is the water dissociation rate constant, C_{H_2O} is the concentration of water in the interphase and λ is the thickness of the interphases. The subscripts H^+, OH^- and H_2O refer to H^+, OH^- ions and water, respectively.

The water dissociation rate constant k_d for pure water at 25°C is given in the literature as $2.5 \times 10^{-5}\ s^{-1}$.

According to eqn [4], the maximum fluxes J_{H^+} and J_{OH^-} from a bipolar membrane that has a 1 nm thick interphase of pure water would be $1.4 \times 10^{-13}\ mol\ cm^{-2}\ s^{-1}$.

The electrical current I through the bipolar membrane is proportional to the sum of all ion fluxes and is given by:

$$I = F(J_{H^+} + J_{OH^-}) \qquad [5]$$

Thus, the maximum current density through a bipolar membrane is, according to eqns [4] and [5], approximately $1.4 \times 10^{-8}\ A\ cm^{-2}$. A current density exceeding this value would lead to a depletion of ions in the interphase and thus to a drastic increase in its electrical resistance. In practice, however, bipolar membranes can be operated at current densities in excess of 0.1 $A\,cm^{-2}$, as demonstrated in **Figure 3A**, which shows the current through a bipolar membrane as a function of the applied voltage. When an increasing voltage difference across a bipolar membrane is established, the current hardly increases until the voltage drop reaches a value of about 0.8 V, corresponding to the concentration potential calculated by eqn [2] for a pH value difference between the two solutions outside the bipolar membrane of about 14. A further small increase in the voltage then leads to a drastic increase in the current density to values in excess of 0.2 $A\,cm^{-2}$. Thus, the current–voltage curves determined with bipolar membranes show two plateau values that indicate a limitation in the current with increasing voltage drop across the membrane, as depicted in Figure 3B. The first plateau value indicates a limitation of the current density due to a limitation of ions in the interphase. However, at 0.8 V accelerated water dissociation begins and the current

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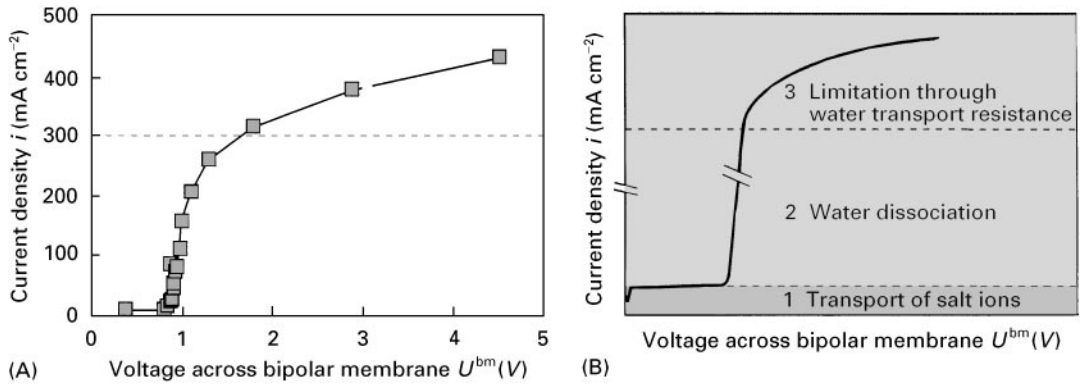

Figure 3 Schematic diagram of the current density as a function of the applied voltage (A) determined with a typical commercially available bipolar membrane and (B) three distinct areas of operation with bipolar membranes.

is no longer limited by a lack of ions until the second plateau value is reached at *ca.* 0.2 A cm^{-2}. Water dissociation is then limited by the supply of water to the interphase.

Thus, there are three distinct regions in the operation of a bipolar membrane. In the first region the current is very low and mainly transported by salt ions. In the second region, high water dissociation occurs and the current is transported by protons and hydroxide ions generated in the interphase. In the third region the production rate of protons and hydroxide ions is limited by the water transport rate into the interphase. Operation of bipolar membranes at current densities that exceed the second plateau value leads to destruction of the membrane.

The experimentally determined current densities indicate that the simple model of a bipolar membrane depicted in Figure 1 is incorrect. Either the water dissociation rate is faster by several orders of magnitude in the bipolar membrane than in free solution or the interphase is much thicker. A thick interphase, however, would lead to a high area resistance of the interphase, which is not the case. From scanning electron microscope photographs and calculations based on the Poisson and Bolzmann relation for the space charge at an interphase between differently charged ion exchange membranes, it can be concluded that the thickness of the interphase is less than 5 nm. This means that, in bipolar membranes the water dissociation is at least 10^6 times faster than in free solution.

Various mechanisms have been suggested to explain the accelerated water dissociation in bipolar membranes. One possible explanation, suggested by Wien, is that at high electric field densities the ion mobility as well as the degree of dissociation of weakly dissociated electrolytes increases with increasing field density. The increase in the dissociation constant of weak electrolytes by the electric field effect can be expressed by an increase in the water dissociation rate constant, assuming that the recombination rate of H^+ and OH^- ions is unaffected.

Other theoretical considerations and experimental evidence support a hypothesis that the accelerated water dissociation is caused by a reversible proton transfer reaction between charged groups and water. This means that, in the presence of certain ionic groups, the water dissociation rate constant may be several orders of magnitude higher than in pure water. In the case of the bipolar membrane the anion exchange groups of the membrane polymer adjacent to the interphase layer are assumed to react with the water molecules at the membrane surface as follows:

$$B + H_2O \underset{k_{-2}}{\overset{k_2}{\Leftrightarrow}} BH^+OH^- \quad \text{and}$$

$$BH^+ + H_2O \underset{k_{-3}}{\overset{k_3}{\Leftrightarrow}} B + H_3O^+ \qquad [6]$$

where B is a neutral base, e.g. a tertiary ammonium group.

Both models can explain the acceleration of the water dissociation in the interphases between the anion and cation exchange layer of the bipolar membrane and serve as theoretical basis for the development of bipolar membranes.

The Preparation and Performance of Bipolar Membranes

The properties required of bipolar membranes to be useful in practical applications are low electrical resistance at high current density, high water dissociation rates, low co-ion transport rate, high ion selectivities, good thermal and, most importantly, good chemical stability since the cation-selective layer of the bipolar membrane is in direct contact with an

acid and the anion exchange layer with an alkaline solution.

Low electrical resistance of the cation and anion exchange layer of the bipolar membrane can be obtained by using a strong acid, such as sulfonic acid groups, and a strong base, such as quaternary ammonium groups as fixed charges in high concentrations in the polymer matrix. To minimize the resistance of the interphase between the cation- and the anion-selective layers the thickness of this interphase must be as thin as possible, as indicated earlier. There are various ways to prepare bipolar membranes with satisfactory properties. Most commonly, membranes are prepared as laminates with some kind of interphase which forms a transition region where the actual water dissociation takes place. In some membranes heavy metal hydroxides are deposited in the interphase to catalyse the water dissociation. However, tertiary ammonium fixed-charge groups at the surface of the anion exchange membrane seem to have the same effect.

A bipolar membrane with satisfactory properties can be prepared, e.g. as a laminate of highly permselective anion and cation exchange layers which have good alkaline and acid stability. An anion-selective layer with the required properties can be obtained by reacting chloromethylated polysulfone dissolved in *n*-methyl pyrrolidone with the monoquaternary salt of 4,4′-diazabicyclo-[2.2.2]-octane. The cation-selective layer can be prepared by introducing sulfonic acid groups as fixed charges into a polyether-ether-ketone matrix using chlorosulfonic acid. The co-ion transport and the swelling behaviour can be controlled in both layers by partial cross-linking. The properties of ion exchange membranes prepared following the above procedures are listed in **Table 1**.

The Performance of Bipolar Membranes

Bipolar membranes are usually characterized in terms of their water dissociation capability, their resistance and their long-term stability. The water dissociation rate and electrical resistance of a membrane prepared by the procedure described above is shown in Figure 3A. Here the current density is shown as a function of the potential drop across the membrane. The test solutions in both compartments adjacent to the bipolar membrane are 1 molar Na_2SO_4. The results indicate that the current density is extremely low at potential differences of less than *ca.* 0.8 V. Then the current density increases up to 0.250 A cm^{-2} with very little increase in voltage drop. When this value is exceeded, the resistance of the membrane increases drastically, due to limitations in the water transport into the interphase region.

Table 1 Electrochemical properties of the cation- and anion-selective layers of a bipolar membrane prepared by the technique described above

	Anion exchange layer	*Cation exchange layer*
Ion exchange capacity (mmol g^{-1})	1.2	1.0
Membrane thickness (μm)	60	60
Area resistance (Ω cm^2)	1.05	1.31
Permselectivity (%)	97.5	98.5
Swelling (%)	8	12.5

Problems in Practical Applications of Bipolar Membranes

Electrodialytic dissociation of water with bipolar membranes is economically very attractive for creating acids and bases. There are, however, several severe problems in practical applications, such as the contamination of the products by salts and low current efficiency at high acid and base concentrations.

Salt contamination of the products is related to the properties of the bipolar membrane. The poor current efficiency is the consequence of the proton and hydroxide ion transport in monopolar membranes, as indicated in **Figure 4**, which illustrates the conversion of Na_2SO_4 into H_2SO_4 and NaOH by electrodialytic water dissociation. Figure 4(A) shows the ion transport in the bipolar membrane. What is desired is a flux of H^+ and OH^- ions from the interphase of the bipolar membrane as the result of the water dissociation. However, in addition there is a flux of Na^+ and SO_4^{2-} ions through the bipolar membrane due to incomplete permselectivity of the anion and cation exchange layers. This leads to a contamination of the base by SO_4^{2-} ions and the acid by Na^+ ions. Since the permeability of the ion exchange layers to SO_4^{-} and Na^+ increases with increasing acid and base concentration, the contamination is also increasing with increasing concentration, as shown in Figure 4B. This figure shows the salt contamination in sulfuric acid and sodium hydroxide produced by water dissociation in bipolar membranes from a 1 mol L^{-1} Na_2SO_4 solution as a function of the concentration of the acid and base produced.

The current efficiency in water dissociation with bipolar membranes is mainly affected by the properties of the anion exchange membrane which has very poor retention of the protons, as illustrated in Figure 4C. The transport mechanism of protons is based on a tunnelling mechanism, with the consequence that protons can permeate the anion

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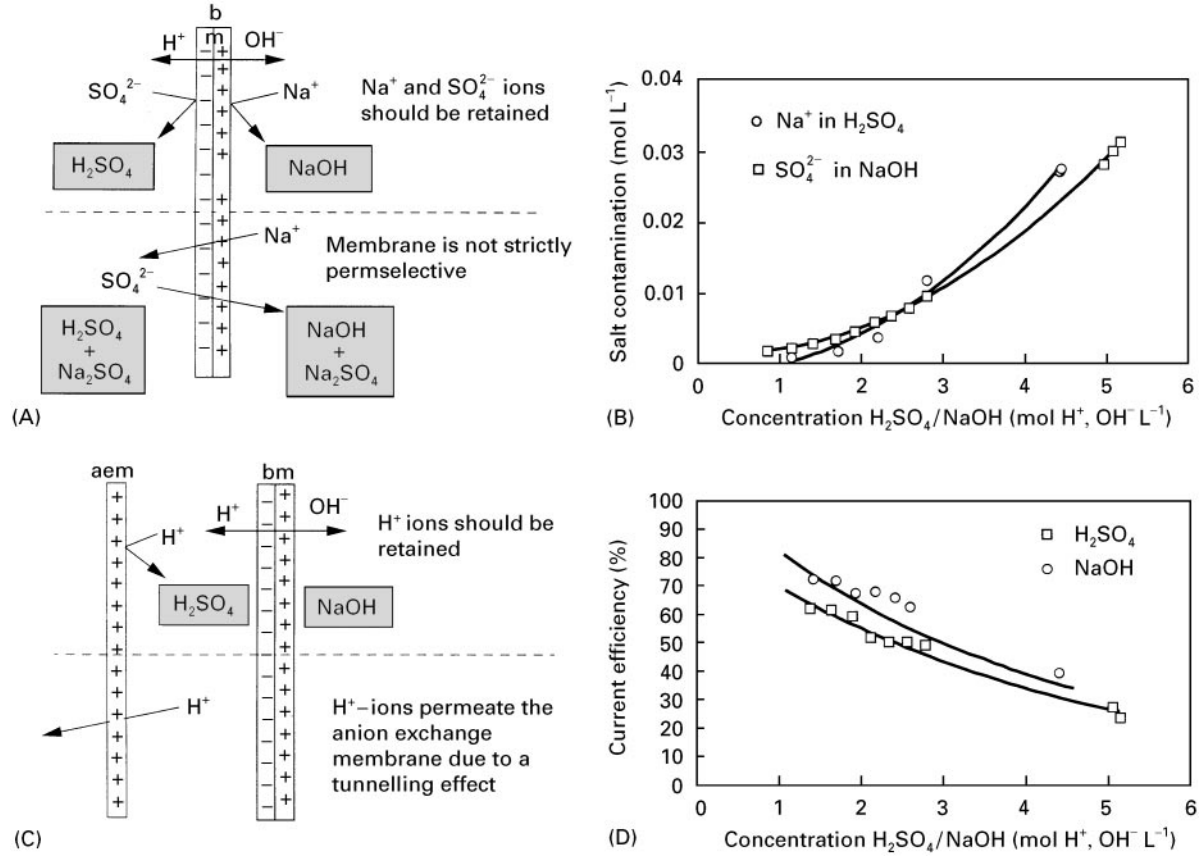

Figure 4 Schematic diagram illustrating (A) the contamination of an acid and a base by salt to incomplete permeability of the cation and anion exchange layers of a bipolar membrane; (B) experimentally determined salt contamination as a function of the acid and base concentrations; (C) the decrease in current efficiency during the production of acids and bases due to the poor acid-blocking capability of the anion exchange membrane; (D) experimentally determined current efficiency as a function of the produced acid and base concentration.

exchange membrane rather freely. The same is true for the hydroxide ions which can permeate the cation exchange membrane. The net result of the process is that protons and hydroxide ions generated in the bipolar membrane neutralize each other. The proton and hydroxide fluxes and thus the current efficiency depend on the concentration, as shown in Figure 4D. With increasing acid and base concentration, the current efficiency decreases rapidly.

Application of Bipolar Membranes

One interesting application of bipolar membranes is the production of caustic soda. Currently, caustic soda is produced as a co-product of the products of chlorine by electrolysis of salt. The worldwide demand for polyvinyl chloride and other chlorinated hydrocarbons has led to the development of a large market for chlorine. Because of environmental problems caused by chlorinated hydrocarbons and the disposal of polyvinyl chloride wastes, the demand for chlorine is steadily decreasing, however, and it can be expected that the demand for caustic soda will soon exceed that produced in the chlorine alkaline electrolysis. Thus interest in alternative processes for obtaining caustic soda is increasing. Electrodialytic water dissociation with bipolar membranes is one of the more promising techniques for the future large scale economic production of caustic soda. However, today's bipolar membranes produce caustic soda with some salt contamination. The production of NaOH and H_2SO_4 from the corresponding salts has been investigated in great detail. Test results obtained in laboratory studies are shown in Figure 4. These tests were carried out with a 1 mol L^{-1} solution Na_2SO_4 feed at room temperature and an applied current density of 0.1 A cm^{-2}. The test results indicate that up to three normal acid and base solutions can be achieved with a current utilization of 60–70%. However the produced acid and base are contaminated by salt and the salt contamination increases with increasing acid and base concentrations due to decreasing

selectivity of the bipolar membrane with increasing acid or base concentrations. Salt concentration can reach values in excess of 0.03 mol L^{-1} at 4 molar base or acid concentrations. To improve the overall efficiency of the electrodialytic dissociation processes and to obtain less salt contamination in the acids and base produced, better proton-blocking membranes have to be developed in addition to more selective bipolar membranes.

Fortunately, there are a large number of other potential applications of the electrodialytic water dissociation where the purity of the product, i.e. the produced acid or base, is not critical and traces of salts can be tolerated. Typical applications of bipolar membranes with large industrial relevance are:

- Recovery of acids and bases such as sulfuric, hydrochloric or hydrofluoric acid and sodium hydroxide from the salts generated in neutralization reactions
- The recovery of organic acids such as formic, acetic, citric, lactic and itaconic acid or certain amino acids from fermentation broths
- Adjustment of pH values in fermentation or chemical production processes without increasing the ion potential
- Regeneration of H_2SO_4 and NaOH from Na_2SO_4 obtained in industrial effluents, for example, in the production of viscose or regenerated cellulose
- Regeneration of acids and bases from scrubbers used to remove SO_2, NO_x from contaminated air streams.

This list of potential applications of the electrodialytic water dissociation with bipolar membranes is not complete and as more efficient bipolar membranes become available, more applications will certainly be identified. In this outline three typical examples for the use of bipolar membranes are described in more detail.

Recycling H_2SO_4 and Dimethylisopropylamine from an Acid Scrubber

Alkaline or acid scrubbers are often used to remove components that are harmful to the environment, such as NO_x, SO_2 or certain amines from waste air streams. In these processes large amounts of acids or bases are consumed and salts are produced. In general, only dilute acids and bases are required in scrubbers. This makes the use of electrodialytic water dissociation with bipolar membranes a very suitable process to recover the acids or bases from the corresponding salts. The recovery of base from scrubbers used to remove SO_2 and NO_x from coal-burning power plants is described in detail in the literature.

Another similar application is the recovery of dimethylisopropylamine removed from a waste air stream by a sulfuric acid scrubber. This type of waste air stream is generated when aluminium casting moulds are made from a sand/epoxy resin mixture by injecting dimethylisopropylamine in a mixture with air as catalyst to cure the resin instantaneously. The amine is not consumed in the process and is emitted in a waste air stream containing *ca.* 0.5 g amine per m^3 waste air. The amine can be recovered as amine sulfate in an acid scrubber, as indicated in **Figure 5**. The amine can then be regenerated by adding sodium hydroxide and distilled. The net result of the process, however, is the production of large amounts of sodium sulfate.

A complete recycling of the amine, the sulfuric acid and water is achieved without the production of a salt by combining the electrodialytic water dissociation with distillation. The process is illustrated in **Figure 6**. The waste air stream containing the amines is fed into an acid scrubber where the free amine is converted into amine sulfate. The effluent of the acid scrubber containing about 10% amine sulfate in a mixture with sulfuric acid is then fed into the electrodialytic water dissociation apparatus

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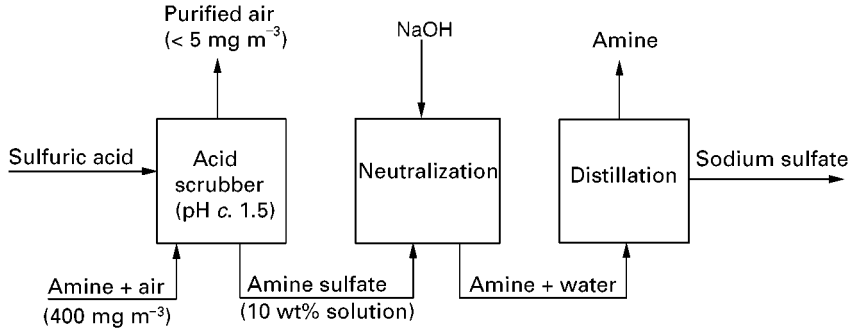

Figure 5 Schematic diagram illustrating a conventional process for recovering an amine from a contaminated air stream using an acid scrubber.

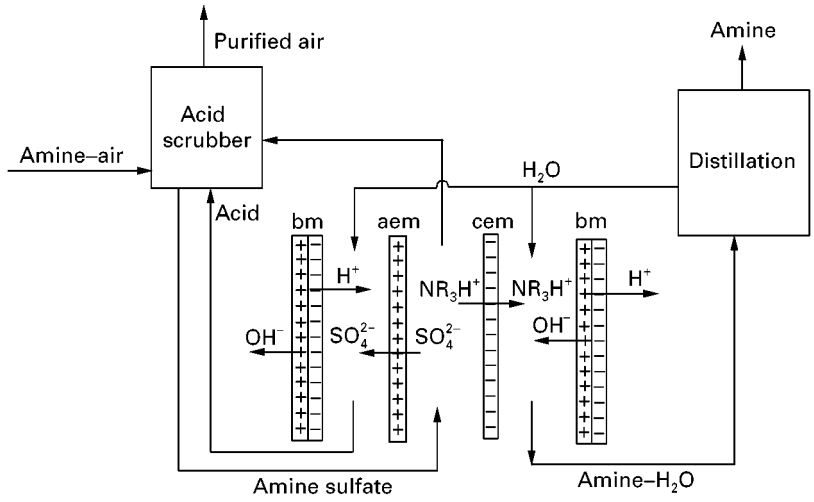

Figure 6 Schematic diagram illustrating the recovery of dimethylisopropyl amine from a waste air stream by combination of acid scrubber, diffusion dialysis and electrodialytic water dissociation using bipolar membranes and distillation.

containing bipolar membranes and anion and cation exchange membranes in alternating series between two electrodes. Here the amine sulfate is converted to the free amine while the sulfate ions form sulfuric acid which is recycled to the acid scrubber. The amine–water mixture is distilled to recover the amine and the water is recycled to the electrodialysis unit. Thus, the process allows complete recovery of the amine from a waste air stream by combination of an acid scrubber and electrodialytic water dissociation.

Production of Itaconic Acid in a Continuous Fermentation Process

One of the more promising applications of bipolar membranes is the adjustment of the pH value of fermentation solutions to recover the organic acids from the spent medium. As an example the production of itaconic acid is described below.

Conventionally, itaconic acid is produced by a batch fermentation process. During fermentation the pH value shifts towards lower values due to the production of the acid. To avoid product inhibition the pH is maintained at a high level by addition of sodium or ammonium hydroxide which form soluble salts with the produced itaconic acid. At the end of the fermentation processes, the free acid is recovered from the spent medium by lowering the pH value by adding sulfuric acid. The adjustment of the pH values in the fermenter as well as in the spent medium is not only costly, but also creates salts mixed with the desired product and thus further purification steps are required. By applying bipolar membrane technology the production of salts can be eliminated and the itaconic fermentation can be carried out more efficiently in a continuous process, as illustrated in the production scheme depicted in **Figure 7**. The flow scheme shows a fermenter combined with an electrodialysis unit fitted with bipolar membranes. The fermenter is continuously fed with substrate and its constituents passed through an ulfiltration unit. The retained biomass is recycled to the reactor while the product containing filtrate is fed to the middle cell of a three-compartment electrodialyser repeating unit. In this cell the solution will be depleted of the ions. The cations, i.e. sodium or ammonium ions, permeate the cation exchange membrane and form, with the OH^- ions generated in the bipolar membrane, NaOH which is concentrated and then fed back into the bioreactor to adjust the pH value. The anions, i.e. the itaconate ions, permeate the anion exchange membrane and form, with protons generated at the bipolar membrane, the itaconic acid which is then concentrated and precipitated. Thus, the itaconic acid is produced in a continuous process without the addition of acids or bases, i.e. without the production of additional salts.

The Electrodialytic Production of Sodium Methylate by Methanol Dissociation

Bipolar membranes may be used not only for the electrodialytic dissociation of water. They can also be applied for the dissociation of alcohol and thus for the production of alcoholates, as illustrated in the following example. Methanol, like water, is both a weak base and a weak acid. Its dissociation constant, however, is somewhat less than that of water. Thus, sodium methanolate can be efficiently produced from methanol and sodium acetate in nonaqueous media by the use of bipolar membranes

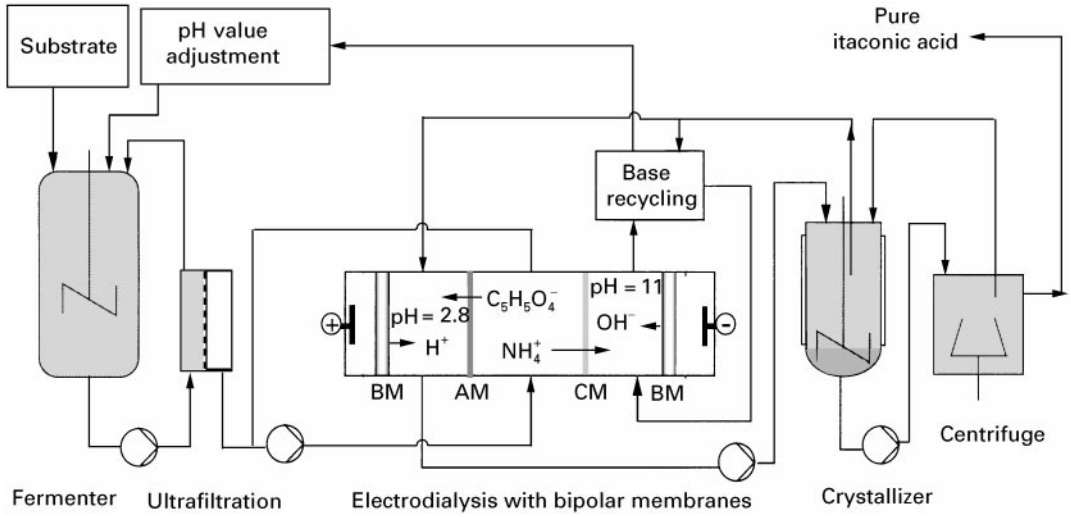

Figure 7 Schematic diagram illustrating a continuous fermentation process for the production of itaconic acid without further addition of acids or bases using bipolar membranes.

according to the reaction scheme illustrated in **Figure 8**, which shows a bipolar membrane electrodialysis stack consisting of two compartment cell systems in a repeating unit between electrodes. Water-free methanol and sodium acetate are fed into the cell formed by the bipolar and the cation exchange membrane which is directed towards the cathode while water-free methanol is passed through the other cell. Under the driving force of an electrical potential gradient, methanol is split in the bipolar membrane into protons and CH_3O^- ions which react with sodium ions migrating from the sodium acetate-containing cell to form CH_3ONa. The acetate ions recombine on the other side of the bipolar membrane with the protons which were produced simultaneously with the CH_3O^- ions in the bipolar membrane to form acetic acid. Thus, sodium acetate and methanol are converted into sodium methanolate. The current efficiency decreases with increasing methylate concentration due to proton transfer from the acetic acid-containing compartment through the bipolar membrane to the sodium methanolate-containing cell. But all in all the process seems to be technically feasible.

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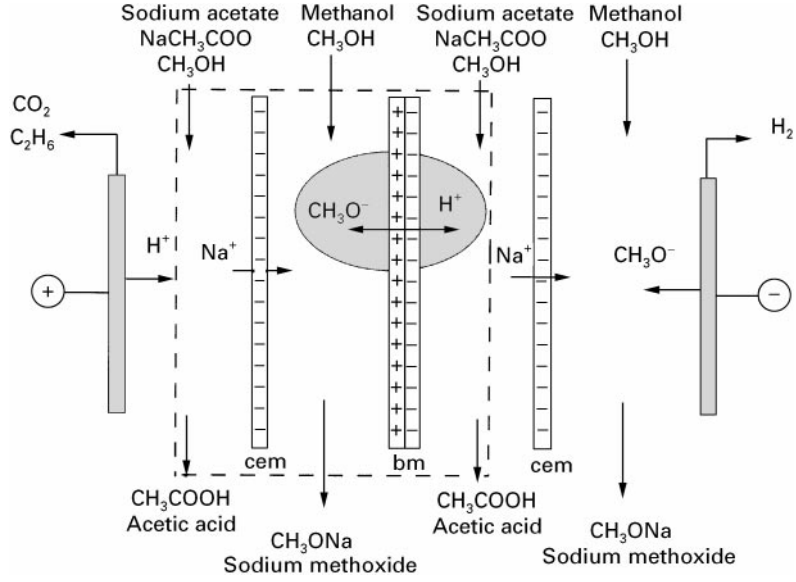

Figure 8 Schematic diagram illustrating the electrodialytic production of sodium methanolate from methanol and sodium acetate in bipolar membranes containing a two-compartment cell unit.

Conclusions

The mechanism of water dissociation in bipolar membranes can be rationalized by a hypothesis which postulates a catalytic reaction between a weak base and water. Based on this hypothesis, very stable chemical and thermal bipolar membranes can be prepared and operated efficiently at current densities in excess of 0.1 A cm^2. The process has many potential applications. There are, however, still a multitude of problems to be solved. Some are related to the poor selectivity of the bipolar membranes and poor acid-blocking capability of the anion exchange membranes; others are caused by the lack of application know-how and practical experience.

Further Reading

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Catalytic Membrane Reactors

M. E. Rezac, Georgia Institute of Technology, Atlanta, GA, USA

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Introduction

The concept of completing both a reaction and separation in a single process unit has motivated research into the development of catalytic membrane reactors. For example, it has long been recognized that palladium metal has the capacity both to permeate hydrogen and to promote a variety of reactions. Thus, harnessing both of these features in a single device seemed a logical combination. In the mid 1960s, Wood and co-workers demonstrated that the dehydrogenation of cyclohexane to cyclohexene could be increased if the hydrogen produced was removed from the reaction vessel through semipermeable palladium walls. In this case, the palladium walls also acted to catalyse the dehydrogenation reaction. A membrane reactor of this type is illustrated in **Figure 1**.

In Russia, Gryaznov conducted much of the research that followed. Starting in the late 1970s, Gryaznov began publishing his results on the use of palladium membrane reactors both to produce and to recover hydrogen from a myriad of dehydrogenation reactions. In the dehydrogenation reactions, hydrogen leaves the reactor by permeating through the semipermeable membrane. However, reactors can also be used in reactions where hydrogen or other reaction products enter the reaction chamber by penetration through the membrane. The commonest classes of reactions that have been successfully influenced by the use of membrane reactor technology are listed in **Table 1**. Details relating to the large volume of research reported are provided in the Further Reading section. None of these membrane reactors are in commercial use. But some – the selective oxidation of methane, for example – are the subject of a very large industrial research effort. If successfully developed, this process would change the feedstock basis of a number of petrochemical processes.

Most research on the development of membrane reactors involves the use of these devices to shift equilibrium-limited reactions (often dehydrogenations). The thermodynamic equilibrium of the reactants and products at the temperature and pressure of the reaction determine the conversion achievable in any given reaction. For dehydrogenation reactions, increasing temperature and decreasing pressure promote an enhanced reaction. Unfortunately, each of these solutions has an associated cost. Increasing the reaction temperature typically results in a reduced

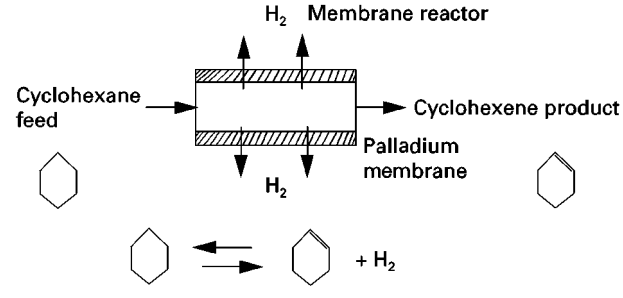

Figure 1 Schematic of a membrane reactor using hydrogen-permeable palladium membranes to shift the equilibrium of the dehydrogenation reaction cyclohexane to cyclohexene.